[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Vapor Phase Photolysis of (+)2-Methylbutanal–Iodine Mixtures at Wave Length 3130 Å.

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Vapor phase photolyses of (+)2-methylbutanal–iodine mixtures are made in 3130 Å. light. The quantum yields of the major products, carbon monoxide, ethylene and 2-iodobutane, are relatively insensitive to changes in temperature and iodine concentration. The importance of two primary processes at 3130 Å. is indicated: $CH_3CH_2CH(CH_3)CHO + h\nu \rightarrow CH_3CH_2CHCH_3 + CHO$ (I); $CH_3CH_2CH(CH_3)CHO + h\nu \rightarrow C_2H_4 + CH_3CH_2CHO$ (II). The 2-iodobutane product is optically inactive. The results are consistent with a planar configuration of the *sec*-butyl free radical or a pyramidal form which has an inversion frequency which is rapid compared to the fast reaction of *sec*-butyl radicals with iodine ($\nu > 4 \times 10^7$ sec.$^{-1}$).

It has been demonstrated recently that the photolysis of 2-methylbutanal at 3130 Å. is an efficient source of *sec*-butyl radicals[1]; however, the proposal of several primary photodecomposition modes was necessary to explain all of the photolysis results

$$
\begin{aligned}
CH_3CH_2CH(CH_3)CHO + h\nu \longrightarrow & \\
& CH_3CH_2CHCH_3 + CHO \quad \text{(I)}\\
& \longrightarrow C_2H_4 + CH_3CH_2CHO \quad \text{(II)}\\
& \longrightarrow CH_3 + C_3H_6CHO, \text{ or} \quad \text{(III)}\\
& CH_4 + CH_2{=}CHCHO \quad \text{(III}'\text{)}\\
& \longrightarrow n\text{-}C_4H_{10} + CO \quad \text{(IV)}
\end{aligned}
$$

Processes I and II were considered important modes of photodecomposition ($\phi_I \cong 0.8$; $\phi_{II} \cong 0.2$), while III and/or III′ was of minor importance ($\phi_{III} \cong 0.04$). The extent of IV could not be estimated.

There were two major points of interest which stimulated the study of the iodine-inhibited photolysis of (+)2-methylbutanal. First, the results should provide a critical test of the suggested primary processes. Previous work, primarily that of Blacet and co-workers,[2] has demonstrated the usefulness of iodine-inhibition technique in the determination of the nature of the primary processes in the photolysis of aldehydes and ketones. By analogy with these studies one expects that the occurrence of process I in the aldehyde–iodine mixtures would be followed by reactions 1 and 2

$$CH_3CH_2CHCH_3 + I_2 \longrightarrow CH_3CH_2CHICH_3 + I \qquad (1)$$

$$HCO + I_2 \longrightarrow CO + HI + I \qquad (2)$$

while III would lead ultimately to CH_3I and IC_3H_6CHO in similar reactions. Presumably the intramolecular processes II, III′ and IV would be unaffected by the presence of iodine. If deactivation of the electronically excited aldehyde molecule by iodine is unimportant for this system and the iodine concentration is sufficient to trap all of the free radicals formed, then the quantum yields of the products, C_4H_9I, C_2H_4, CH_3I, CH_4 and C_4H_{10} would be measures of the primary efficiencies of processes I, II, III, III′ and IV, respectively.

This study also was designed to gain information about the configuration of the gaseous alkyl free radical. In theory alkyl free radicals have either a planar or pyramidal form. Theory and experiment have not yet given an unambiguous answer to the problem. The first theoretical work suggested that the methyl free radical is planar in its ground state.[3,4] More recently several investigators have concurred in the conclusion that the most stable methyl radical configuration is pyramidal.[5] The vacuum ultraviolet absorption spectrum of the methyl free radical has not been sufficiently resolved to define the configuration unambiguously.[6] Chemical evidence of radical configuration is inconclusive at present.[7]

The compound studied in this work, (+)2-methylbutanal, contains an asymmetric center. It is capable in theory of producing an asymmetric *sec*-butyl free radical on absorption of radiation, provided that the ground state of the radical is pyramidal and that the potential barrier to inversion is sufficient to resist racemization as process I occurs. It is likely that the *sec*-butyl free radical is formed in its ground state on absorption of 3130 Å. light, since the energy absorbed is near the minimum necessary to break the C_4H_9–CHO bond. In the iodine-inhibited photolysis of 2-methylbutanal one expects that reaction 1 will occur on almost every collision between *sec*-butyl radicals and iodine molecules; the very high rate of reaction between CH_3 and I_2 leads one to this view.[8] The observation of optical activity in the 2-iodobutane formed in this reaction would prove the pyramidal form of the *sec*-butyl free radical. A planar radical would lead to optical inactivity of the product, but this result would fail to distinguish between the two possible configurations since the inversion frequency of the pyramidal form might be very rapid. Walsh[5b] predicts that the potential barrier to inversion in CH_3 may be considerably less than that for NH_3 (2076 cm.$^{-1}$), so a rapid inversion frequency is anticipated. Experiments in which asymmetric free radicals were generated in the solution phase usually have given an inactive product.[7] However, the same result was not expected *a priori* for the experiments in the gaseous state, since the inversion frequency

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[1] J. T. Gruver and J. G. Calvert, THIS JOURNAL, **78**, 5208 (1956).

[2] For references to the earlier work see, F. E. Blacet and J. N. Pitts, Jr., *ibid.*, **74**, 3382 (1952).

[3] (a) J. H. Van Vleck, *J. Chem. Phys.*, **1**, 177, 219 (1933). **2**, 20 (1934).

[4] (a) W. G. Penney, *Trans. Faraday Soc.*, **31**, 734 (1935); (b) H. H. Voge, *J. Chem. Phys.*, **4**, 581 (1936); (c) A. D. Walsh, *Disc. Faraday Soc.*, **2**, 18 (1947).

[5] (a) J. W. Linnett and A. J. Poe, *Trans. Faraday Soc.*, **47**, 1033 (1951); (b) A. D. Walsh, *J. Chem. Soc.*, 2296 (1953); (c) T. Itoh, K. Ohno and M. Kotani, *J. Phys. Soc. Japan*, **8**, 41 (1953).

[6] G. Herzberg and J. Shoesmith, *Can. J. Chem.*, **34**, 523 (1956).

[7] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 25.

[8] E. Horn, M. Polanyi and D. W. G. Style, *Trans. Faraday Soc.*, **30**, 189 (1934).

of a non-planar radical may be significantly larger in solution than in the dilute vapor phase as a consequence of the very high collision frequency and the perturbing influence of the strong forces operative in the condensed phase.

Experimental

Apparatus.—The photolysis system consisted of an all-quartz cell, 150 mm. long and 31 mm. diameter, a trap and a ground-glass valve which was opened and closed with a solenoid. This system was isolated from stopcocks by mercury valves and was contained in a thermostated box. The thermostat was heated to a temperature of 48° or higher (to prevent condensation of iodine) and regulated to ∓1° by a thermoswitch in series with a cone heater. Radiation from a Hanovia type A (S-500) burner, operated on a regulated 3 amp. a.c. current, was filtered to isolate wave length 3130 Å.[9] The light beam was collimated by a lens to give a fairly homogeneous beam of radiation that filled the cell volume (113 cc.) almost completely. Absolute intensities were estimated by acetone vapor photolysis (at temperatures near 110°) before each photochemical run. The fraction of light absorbed was found with a photomultiplier circuit.

In runs which were made to synthesize a quantity of 2-iodobutane for polarimetric study, a General Electric AH-6 quartz-jacketed, water-cooled arc was used as a light source. The combination of a dilute solution of potassium chromate and a Corning 9863 filter replaced the usual filter system; this isolated a band of radiation of large intensity in the range 3100–4000 Å. Only the region from 3100–3300 Å. was absorbed by the aldehyde. The small photolysis cell was replaced with a 22-l. cell made from a round bottomed flask with a quartz window connected to the neck of the flask through a graded-seal. With this system a mixture of 8 mm. of aldehyde and 3 mm. of iodine at 60° yielded sufficient iodide in a 6 hr. run (without serious depletion of the iodine and aldehyde reactants during the course of the experiment) to enable accurate determination of the optical rotation (about 0.1 cc.).

Materials.—(+)2-Methylbutanal was prepared as described previously.[1] (+)-Iodobutane was made from (−)2-butanol[10] by the reaction with PI_3.[11] All standard gases were Phillips research grade.

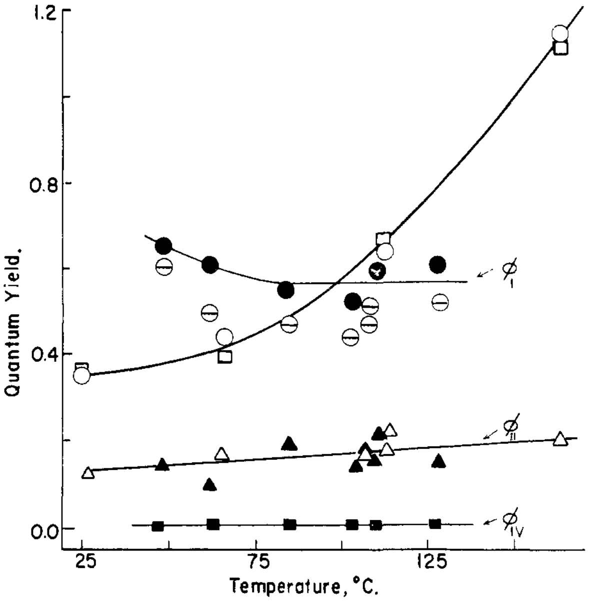

Fig. 1.—Temperature dependence of the quantum yields of the major products of the iodine-inhibited and the uninhibited photolyses of 2-methylbutanal at 3130 Å.: products of the uninhibited photolysis, CO, ○; n-C_4H_{10}, □; C_2H_4, △; products of the iodine-inhibited photolysis, CO, ●; n-C_4H_{10}, ■; C_2H_4, ▲; sec-C_4H_9I, ⊖; $[C_4H_9CHO] = 1.4 \times 10^{-3}$ M; in the iodine-inhibited runs, $[I_2] = 5 \times 10^{-5}$ M; the curves laveled ϕ_I, ϕ_{II}, ϕ_{IV}, represent the best estimates of the primary efficiencies of the processes I, II and IV, respectively.

Product Analysis.—After photolysis the products were removed from the system in three fractions. The first fraction, carbon monoxide, was removed with a Toepler pump while the remaining products and excess aldehyde and iodine were condensed in the trap at liquid nitrogen temperature. The second fraction, ethylene and n-butane, was pumped out with the trap at Dry Ice–acetone temperature. Nitrogen was introduced until the pressure in the system was that of the atmosphere. Then the trap which contained the product 2-iodobutane, excess aldehyde and excess iodine, was cut from the system. The iodine was removed by the addition of mercury, and volatile materials that remained in the trap were vacuum distilled to one arm of a U-tube and allowed to vaporize and contact potassium hydroxide pellets contained in the other arm. After 10–16 hours most of the aldehyde had polymerized, and any hydrogen iodide had reacted. The remaining volatile material, primarily 2-iodobutane as identified by mass spectrometry, was distilled to a small sample tube and washed into an erlenmeyer flask with acetic acid. Enough acetic acid was added to the flask to give a total volume of about 35 cc. To this was added about 2 g. of sodium acetate and enough bromine to turn the solution dark orange. The solution was allowed to stand for one hour to ensure the complete replacement of iodide and ultimate oxidation to iodate. It was then heated to remove the excess bromine, cooled to room temperature, distilled water was added to a volume of 50 cc., 1 g. of potassium iodide was added and the solution was titrated with standard sodium thiosulfate (0.005 N). Runs with standard mixtures of iodide and aldehyde showed that at least 90% of the alkyl iodide was recovered using the procedure described. The reported quantum yields of the 2-iodobutane product are probably about 10% low. Carbon monoxide was analyzed chemically by use of a Blacet–Leighton gas analysis system. All other products were determined with a General Electric analytical mass spectrometer.

The procedure as described above was modified slightly to isolate the iodide for the determination of its optical rotation. In this case the product which remained after the aldehyde polymerization over potassium hydroxide (about 0.1 cc. of iodide) was transferred to a micro-polarimeter tube (0.2 ml. volume), enough carbon tetrachloride was added to fill the tube completely and the rotation was determined at 5460 Å. on a Rudolph, Model 200, Photoelectric Polarimeter. Then the chemical analysis for iodide was made as before. Standard samples of (+)2-iodobutane were subjected to the entire separation procedure; no significant racemization of the iodide occurred and at least 90% of the original amount of iodide was recovered. Standard samples of (+)2-methylbutanal were treated by the polymerization procedure described; practically all of the aldehyde was removed, and there was no measurable rotation of the small amount of the aldehyde which remained unpolymerized.

Products.—The quantum yields of the products of the 3130 Å. iodine-inhibited photolyses of 2-methylbutanal are given in Table I. These results and those of the uninhibited photolyses[1] are compared in Fig. 1.

Determination of the Optical Activity of the 2-Iodobutane Product.—The average observed rotation of the 2-iodobutane product was $+0.01_6 \pm 0.01°$. With complete retension of the activity in the iodide product, the observed rotation would have been approximately 3.5°, considering the degree of purity of the original reactant aldehyde and extent of dilution for analysis. Thus within the error of these experiments the 2-iodobutane product is optically inactive.

Discussion

Primary Processes in 2-Methylbutanal Photolysis at 3130 Å.—The results confirm the occur-

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[9] R. E. Hunt and W. Davis, Jr., THIS JOURNAL, **69**, 1415 (1947).

[10] (−)2-Butanol was provided by Professor George Helmkamp, University of California, Riverside.

[11] M. C. Berlak and W. Gerrard, *J. Chem. Soc.*, 2309 (1949).

TABLE I

QUANTUM YIELDS OF THE PRODUCTS OF THE IODINE-INHIBITED PHOTOLYSIS OF (+)2-METHYLBUTANAL AT 3130 Å.

Run no.	Temp., °C.	P_{I_2}, mm.	$P_{C_4H_9CHO}$, mm.	Product quantum yields CO	 n-C_4H_{10}	 C_2H_4	 sec-C_4H_9I
1	48.0	0.9	23.4	0.66	0.002	0.14	0.61
2	61.5	3.5	27.2	.61	.002	(.10)	.50
3	84.0	3.4	25.7	.56	.007	.19	.47
4	102.0	3.0	27.9	.53	.005	.14	.45
5	107.1	25.9	33.3	.51	.001	.17	.48
6	107.4	8.0	34.3	(.42)	.001	.17	.53
7	109.5	3.5	34.9	.61	.002	.15	(.39)
8	127.5	2.2	32.8	.61	.011	.16	.53

rence of the following primary processes and secondary reactions

$$CH_3CH_2CH(CH_3)CHO + h\nu \longrightarrow CH_3CH_2CHCH_3 + HCO \quad (I)$$

$$\longrightarrow C_2H_4 + CH_3CH_2CHO \quad (II)$$

$$\longrightarrow n\text{-}C_4H_{10} + CO\ (\text{minor}) \quad (IV)$$

$$CH_3CH_2CHCH_3 + I_2 \longrightarrow CH_3CH_2CHICH_3 + I \quad (1)$$

$$HCO + I_2 \longrightarrow CO + HI + I \quad (2)$$

The consistency of the results with this mechanism can be seen from the information summarized in Fig. 1. The open symbols represent the products of the uninhibited photolysis[1]; the darkened symbols show the products from the experiments with added iodine.

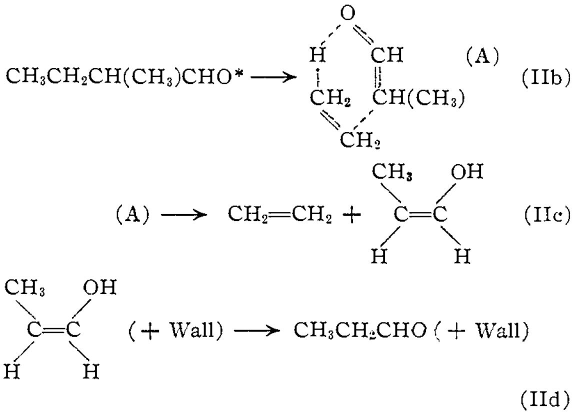
(a) **Primary Processes I and IV.**—Very marked changes are evident in the quantum yields of carbon monoxide and butane. In the uninhibited runs Φ_{CO} (○) and $\Phi_{C_4H_{10}}$ (□) are near equal and show evidence of the formation of carbon monoxide and butane in a chain process. In runs with added iodine, butane (■) is practically absent and the yield of carbon monoxide (●) is large and nearly temperature independent. Accompanying the decrease in the $\Phi_{C_4H_{10}}$ with iodine addition is the appearance of the new product, 2-iodobutane (⊖). *sec*-Butyl radical formation in I and the unimportance of IV are established by these results. If the iodide and carbon monoxide are formed only in the reaction scheme I, IV, 1 and 2, then we expect $\Phi_{CO} = \Phi_{sec\text{-}C_4H_9I} + \Phi_{C_4H_{10}}$. If account is taken of the fact that the procedure for iodide analysis results in about a 10% loss of the iodide, then the data are entirely consistent with this expected relationship.

Indirect proof of the occurrence of radical combination reactions of HCO (*e.g.*, $HCO + C_4H_9 \rightarrow C_4H_9CHO$) in the uninhibited photolysis is had in the fact that Φ_{CO} is significantly larger in the inhibited photolysis than in the uninhibited photolysis at 48°.

(b) **Primary Process II.**—The relative insensitivity of the quantum yields of ethylene to change in temperature and presence of iodine is apparent from Fig. 1. The yields without iodine (△) determine within the experimental error the same curve as those in runs with iodine (▲). This is striking evidence in confirmation of process II. The relative constancy of the quantum yields of the various products with increase in iodine pressure in the range from 1 to 26 mm. suggests that both deactivation of electronically-excited aldehyde molecules by iodine and the chemical reaction of excited molecules with iodine (*e.g.*, $C_4H_9CHO + I_2 \rightarrow C_4H_9I + CO + HI$) are unimportant in this system.

The present results considered in combination with those of McNesby and Gordon[12] give some interesting details of the mechanism of process II. The iodine pressure independence of the quantum yields of ethylene in this work exclude an analog to the mechanism choice of McNesby and Gordon. All of the published information related to the process II in ketone and aldehyde photolyses appears to be consistent with one of the alternative mechanisms of Davis and Noyes.[13] Presumably, electronic excitation of the carbonyl group is followed rapidly by the formation of a transition state (A); the probability of its formation appears to be directly related to the number of γ-H atoms in the absorbing molecule.[14,15] Reaction IIb must follow IIa within a very small interval of time which precludes measurable deactivation of the excited state by iodine. The demonstrated exchange of the α-H atoms in the carbonyl product[12] is striking evidence for the enol-form of the carbonyl molecule in IIc; it excludes the alternative mechanism of γ-H transfer directly to the α-C atom.[13] Recently Manning[16] has given some theoretical justification of the mechanism choice, IIa, b, c, d. A critical test of this mechanism is underway in these laboratories. The identification of the suggested enol-form of the carbonyl compound is to be attempted by analysis without condensation of the photolysis products using long-path infrared absorption spectroscopy.[17]

$$CH_3CH_2CH(CH_3)CHO + h\nu \longrightarrow CH_3CH_2CH(CH_3)CHO^* \quad (IIa)$$



$$CH_3CH_2CH(CH_3)CHO^* \longrightarrow (A) \quad (IIb)$$

$$(A) \longrightarrow CH_2{=}CH_2 + CH_3(H)C{=}C(H)OH \quad (IIc)$$

$$CH_3(H)C{=}C(H)OH\ (+\ \text{Wall}) \longrightarrow CH_3CH_2CHO\ (+\ \text{Wall}) \quad (IId)$$

Other Possible Primary Processes.—No evidence is found for the occurrence of either of the alternative primary processes, III and III′, suggested previously. The expected products of these reactions, CH_3I and CH_4, could not be detected. It is possible that the methane formation in the low temperature uninhibited photolyses of 2-methylbutanal arises from the decomposition of a vibrationally excited molecule formed by internal conversion of the electronic excitation; the lifetime of the vibrationally excited molecule may be

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[12] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **80**, 261 (1958).

[13] W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **69**, 2153 (1947).

[14] T. W. Martin and J. N. Pitts, Jr., *ibid.*, **77**, 5465 (1955).

[15] J. W. Kraus and J. G. Calvert, *ibid.*, **79**, 5921 (1957).

[16] P. P. Manning, *ibid.*, **79**, 5151 (1957).

[17] Joint research with J. N. Pitts, Jr., University of California, Riverside.

sufficient so that rather complete deactivation of the excitation is effected in the experiments with added iodine. The relatively small energy separation of the vibrational modes of molecular iodine are presumed to make it an effective agent to remove vibrational excitation.[18] At each temperature about 20% of the electronically excited molecules formed do not lead to observed products; presumably these are involved in internal conversion processes and are collisionally deactivated.

The Quantum Efficiencies of the Primary Processes in the Butyraldehydes.—The best estimates of the primary quantum efficiencies of the various processes in 2-methylbutanal photolysis at 3130 Å. are shown by the labeled curves in Fig. 1. Because of the inaccuracy in the iodide analysis method, Φ_{CO} was taken as a measure of ϕ_{I}; since IV is unimportant this is justified. The average values for the temperature range 48 to 128° are: $\phi_{I} = 0.60$; $\phi_{II} = 0.17$; $\phi_{IV} = 0.003$. The small temperature dependence of the quantum yield data suggests that ϕ_{I} decreases and ϕ_{II} increases slightly as the temperature is raised. A comparison of the primary efficiencies of photodecomposition of iso- and *n*-butyraldehydes with these results is instructive. For the analogous processes in *n*-butyraldehyde photolysis at 3130 Å., $\phi_{I} = 0.35$ (60–150°); $\phi_{II} = 0.20$ (65–208°); $\phi_{IV} = 0.017$ (60–150°); with isobutyraldehyde at 3130 Å., $\phi_{I} = 0.72$ (60–150°); $\phi_{II} = 0.00$; $\phi_{IV} = 0.03$ (60–150°). The number of γ-H atoms in an aldehyde or ketone reflects qualitatively the probability of the olefin forming intramolecular rearrangements.[15,16] Since this number (3) is the same for *n*-butyraldehyde and 2-methylbutanal, the similarity in the quantum efficiencies of process II for these two aldehydes is not unexpected. Isobutyraldehyde has no γ-hydrogen atoms, and this mode of decomposition is absent. The fact that the primary efficiency of radical formation in isobutyraldehyde and 2-methylbutanal photolyses is much larger than that for *n*-butyraldehyde may be related to the higher stability of the branched isopropyl and *sec*-butyl radicals compared to *n*-propyl radical. The great importance of I compared to IV for photolyses of all the simple aliphatic aldehydes at 3130 Å. appears to be a general rule.[2]

The Configuration of the Gaseous *sec*-Butyl Free Radical.—Within the experimental error the 2-iodobutane product formed in the iodine-inhibited photolyses of 2-methylbutanal is optically inactive. This result does not allow an unambiguous choice of the radical configuration; it indicates that the *sec*-butyl radical is either planar or it is pyramidal with a rate of inversion which is fast compared to the rate of reaction with iodine in our experiments. It is impossible to extrapolate the available information and obtain a realistic estimate of the inversion frequency for a hypothetical pyramidal form of the *sec*-butyl radical.[19] From this work we may derive a rough estimate of the minimum inversion frequency of an assumed pyramidal *sec*-butyl radical. The number of classical collisions of a *sec*-butyl free radical with iodine is about 3.6×10^{7} sec.$^{-1}$ for the conditions of these experiments ($P_{I_2} = 3.0$ mm. at 333°K.; assuming $\sigma_{C_4H_9} = 5.9$ Å.; $\sigma_{I_2} = 4.6$ Å.). The rate of reaction of CH_3 or C_2H_5 with I_2 is near the collision number,[8] and it is a reasonable assumption that reaction 1 also will occur on practically every classical collision between the reactants. Assuming this, we estimate that the frequency of inversion must be greater than 3.6×10^{7} sec.$^{-1}$ to explain the racemic iodide product found in this work. Until some meaningful estimate of the inversion frequency for a hypothetical pyramidal *sec*-butyl is available, a more definitive conclusion regarding the configuration of the *sec*-butyl free radical cannot be derived from this study.

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[18] W. A. Noyes, Jr., *J. Phys. Colloid Chem.*, **55**, 925 (1951).

[19] For a general discussion of the inversion frequency of the ammonia-like molecules, see G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 224.

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